

# **Exhibit “A”**

US007531709B2

(12) **United States Patent**  
**Scalzi et al.**(10) **Patent No.:** **US 7,531,709 B2**  
(45) **Date of Patent:** **\*May 12, 2009**(54) **METHOD FOR ACCELERATED  
DECHLORINATION OF MATTER**(75) Inventors: **Michael Scalzi**, Doylestown, PA (US);  
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(US)(\*) Notice: Subject to any disclaimer, the term of this  
patent is extended or adjusted under 35  
U.S.C. 154(b) by 241 days.This patent is subject to a terminal dis-  
claimer.(21) Appl. No.: **11/423,749**(22) Filed: **Jun. 13, 2006**(65) **Prior Publication Data**

US 2006/0223162 A1 Oct. 5, 2006

**Related U.S. Application Data**(63) Continuation of application No. 10/610,558, filed on  
Jul. 2, 2003, now Pat. No. 7,129,388.(60) Provisional application No. 60/437,983, filed on Jan.  
6, 2003.(51) **Int. Cl.**  
**A62D 3/00** (2007.01)(52) **U.S. Cl.** ..... **588/316**; 588/406; 588/415(58) **Field of Classification Search** ..... 588/313,  
588/315, 316, 318, 319, 320, 402, 406, 415,  
588/261; 423/240 R, 240 S

See application file for complete search history.

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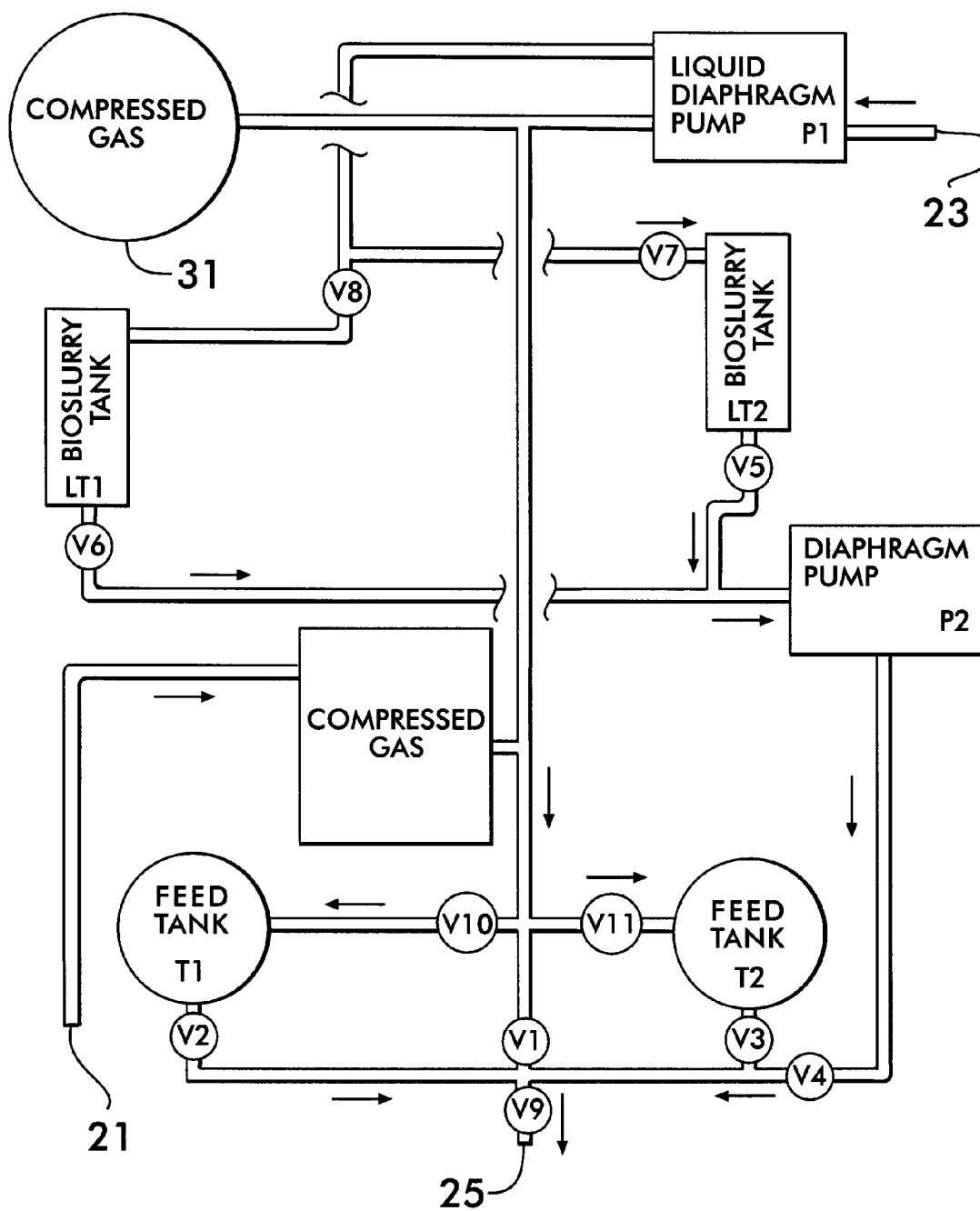
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*Primary Examiner*—Edward M Johnson(74) *Attorney, Agent, or Firm*—Gregory J. Gore(57) **ABSTRACT**Accelerated dechlorination of soil and water contaminated  
with chlorinated solvents is achieved by stimulating anaero-  
bic microorganisms and thus increasing the rate of biological  
mineralization of the solvents. This is accomplished by a  
treatment process consisting of colloidal suspension of metal  
powder, an organic hydrogen donor, chemical oxygen scav-  
engers in solution with essential nutrients, and vitamin stimu-  
lants such as B2 and B12 delivered via compressed gases N or  
CO<sub>2</sub> so as not to oxygenate an environment targeted for  
anaerobic processes. The treatment stimulates naturally  
occurring microorganisms while oxidizing dissolved phase  
target compounds via the surface action of the iron particles  
resulting in the breakdown of chlorinated solvents such as  
tetrachloroethene, trichloroethene, carbon tetrachloride and  
their daughter products.**16 Claims, 1 Drawing Sheet**

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**METHOD FOR ACCELERATED  
DECHLORINATION OF MATTER****RELATED APPLICATION**

This patent application is a continuation of co-pending patent application Ser. No. 10/610,558 filed Jul. 2, 2003 for "Method for Accelerated Dechlorination of Matter" which is related to provisional patent application Ser. No. 60/437,983 entitled "Method for Accelerated Dechlorination of Matter" filed on Jan. 6, 2003, priority from which is hereby claimed.

**FIELD OF THE INVENTION**

The present invention relates to the combined and synergistic utilization of chemicals in conjunction with the biomineralization processes of subsurface soil and groundwater pollutants. More specifically, it relates to an accelerated dechlorination of subsurface matter by anaerobic microorganisms in conjunction with oxygen scavengers, vitamins, nutrients, and zero valent metals.

**BACKGROUND OF THE INVENTION**

Through the years, chlorinated solvents have had a large impact on several industries, including pharmaceuticals, chemical processing, food extraction, dry cleaning, and metal cleaning. With wide spread use and improper handling and storage, extensive soil and water damage has occurred. Due to their toxicity, carcinogenicity, and persistence in the environment, chlorinated solvents are listed by the United States Environmental Protection Agency as high priority pollutants. If left untreated, chlorinated solvents may remain unchanged for a period of fifty years or more. The most common chlorinated solvents used are methylene chloride, tetrachloroethene, trichloroethene, carbon tetrachloride, chloroform, tetrachloroethane, dichloroethene and vinyl chloride. Carbon tetrachloride is a systematic poison of the nervous system, the intestinal tract, the liver, and the kidneys. Vinyl chloride and methylene chloride are known carcinogens, and could also affect the nervous system, the respiratory system, the liver, the blood, and the lymph system.

Chlorinated solvents are often found in separate phases mixtures commonly referred to as dense nonaqueous-phase liquids ("DNAPLs"). DNAPLs are visible, denser-than-water, separate oily phase materials in the subsurface whose migration is governed by gravity, buoyancy, and capillary forces. Chlorinated solvents partition into the water phase to create a dissolved contaminant plume when in contact with water, thus creating a long-term, continuing source of contamination as the soluble constituents slowly dissolve into moving groundwater.

One common technique for treating contaminated matter is the "pump-and-treat" method in which contaminated groundwater is pumped to the surface, cleaned chemically or by passing the groundwater through a bioreactor, and then reinjected into the groundwater. This process is carried out over a long period and various factors complicate the removal of these contaminants from the environment. Also, they are very volatile, highly mobile, denser than water, and generally found in the environment as mixtures of products with different degrees of chlorination. The "pump-and-treat" method is therefore problematic.

The problems with the "pump-and-treat" method can be overcome with the use of anaerobic microorganisms which have the capability to decompose a wide range of highly chlorinated compounds. However, anaerobic microorgan-

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isms are at a disadvantage in that their growth is slow when compared to that of aerobic organisms. In-situ they are at an even greater disadvantage due to the partitioning of the targeted substrates into the soil matrix. There is therefore a need in the art to utilize the ability of anaerobic microorganisms to decompose chlorinated compounds which can be achieved at a faster rate.

**SUMMARY OF THE INVENTION**

The present invention achieves accelerated dechlorination of soil and water contaminated with chlorinated solvents by stimulating anaerobic microorganisms and thus increasing the rate of biological mineralization of the solvents. This is accomplished by a treatment process consisting of a colloidal suspension of metal powder, organic hydrogen donor such as glucose, sucrose, alcohols, propionates, lactates, acetates, chitin, polylactate esters, glycerol tripolylactate, xylitol pentapolyolactate, and sorbitol hexapolyolactate, chemical oxygen scavengers in solution with essential nutrients, and vitamin stimulants such as B2 and B12 delivered via interconnected pneumatic pumps and pressurized vessels driven by compressed gases N or CO<sub>2</sub> so as not to oxygenate an environment targeted for anaerobic processes. The treatment stimulates naturally occurring microorganisms while addressing dissolved phase target compounds via the surface action of the metal particles. The overall effect results in the breakdown of chlorinated solvents such as tetrachloroethene, trichloroethene, carbon tetrachloride and their daughter products. The incorporation of the B12 acts as both an enzymatic stimulus for the anaerobic action and a surface catalyst of the iron particle. Cobalt, the core element of the B12, enhances the surface oxidation of the metal further.

A closed delivery system is used to deliver the process utilizing a combination of gas and liquid delivery systems. All of the vessels are interconnected and valved, allowing for mixings, washings, filling, and discharge of materials via pressure vessels or mechanical pumping systems. The system utilized allows for a variety of dissimilar compounds to be delivered via a single injection line. Further, the switching between feed systems is accomplished without any loss of pressure to the delivery line eliminating the common problems experienced from the vacuum developed down-hole as pressure is released and reapplied. Lastly, the current system is fully self-contained requiring no electrical supply. The only site utility requirement is an available water source for slurry preparation.

One embodiment of the present invention is carried out in the following steps.

**Step 1: Subsurface Pathway Development**

Initially, a gas is delivered to the subsurface via the delivery system further described herein. The gas is used so as not to introduce oxygen into an environment targeted for anaerobic processes. Injection points are advanced via traditional direct push technology or may be permanently installed injection wells. The gas is introduced at a maximum pressure of approximately 175 psi such that delivery pathways and voids are established. Pathway development is verified by observing a substantial pressure drop at the surface monitoring point. Gas introduction is immediately halted once the pressure drop is observed.

**Step 2: Sodium Sulfite Nutrient and Micro Nutrient Injection**

A solution of sodium sulfite and nutrients (nitrogen and ortho-phosphate) is immediately injected into the subsurface pathways and voids that were developed during the gas injection step. Sodium sulfite acts as an oxygen scavenger, iron

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reducer and sulfate source. As an oxygen scavenger, the sodium sulfite prevents the oxidation of the later-injected ZVI by the dissolved oxygen while promoting anaerobic conditions that are favorable for the biodegradation of the CVOCs. Nutrients, injected as organic ammonia and ortho-phosphate, are required for the maintenance of the microbial metabolic pathways, ATP/ADP synthesis and organelle development. Further, the incorporation of the ortho phosphate inhibits acetogenesis, a competing methanogenic reaction which consumes acetate and produces methane.

#### Step 3: Zero Valent Metal Injection

Immediately following the sodium sulfite/bioslurry solution injection, a colloidal suspension of a metal powder is added to an additional quantity of the bioslurry solution and the colloidal suspension is injected to reduce concentrations of dissolved-phase CVOCs while providing for rapidly generated hydrogen, the evolution of hydroxides and as a result overall microbial stimulation and biofilm formation.

#### Step 4: Anaerobic Hydrogen Source Injection

An anaerobic organic hydrogen source is injected immediately after the ZVI injection to provide a slow release hydrogen source for the anaerobic dechlorination of the CVOCs. Vitamin B12 and riboflavin B2 is mixed with the anaerobic stimulating hydrogen source to provide essential micro enzymes at the anaerobic sites.

#### Step 5: Sodium Sulfite/Nutrient Injection

A second injection of the sulfite/nutrient mixture is then performed to clear the injection lines and to provide for in-situ mixing and penetration of the anaerobic stimulating product.

#### Step 6: Post Liquid Injection—Gas Injection

Lastly, the injection lines are cleared of liquids by a second gas injection and all injectants are forced into the created formation and upward into the vadose zone. Once the injection cycle is complete, the injection point is temporarily capped to allow for the pressurized subsurface to accept the injectants. Once back-pressure diminishes, the injection rods are extracted. Injection boring locations are then sealed with bentonite or sand to prevent short-circuiting from adjacent injection locations.

Other objects and advantages of the present invention will be readily apparent to those of skill in the art from the following drawing and description of the preferred embodiment.

### BRIEF DESCRIPTION OF THE DRAWINGS

The FIGURE is an apparatus and flow diagram which describes an in-situ delivery system of the present invention.

### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

According to the preferred embodiment of the invention, the following process and delivery system apparatus is employed. In order to keep an anaerobic environment, nitrogen or carbon dioxide gas is used to propel all injectants into the subsurface. The gas is first injected into the subsurface at a maximum pressure of approximately 175 pounds per square inch until a significant pressure drop is observed at the injection pressure vessel. This process is referred to as delivery pathway development with the intent of opening pathways into the subsurface for the injections. These pathways are believed to be those more permeable pathways along which chlorinated solvents are more likely to have migrated, both in the vadose and saturated zones. Liquid and liquid-entrained

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injectants are then delivered with pressurized gas to the pathways that are produced during the pathway development.

Chemical oxygen scavengers, reducing agents such as sodium sulfite, are then injected to remove oxygen from groundwater and soil moisture immediately after pathway development in the subsurface, facilitating the anaerobic conditions that are preferred for the reductive dehalogenation of chlorinated solvents by indigenous bacteria. The resulting environment contains a wide spectrum of inorganic, biochemical, and enzymatic redox systems. Along with the reducing agents, nutrients such as organic ammonia and ortho-phosphate are added to the injectants in order to support microbial activity.

In an anaerobic environment, zero valent metal is then injected as an additive to the reducing agent bioslurry mixture. Zero valent metals have a moderately low toxicity and a good reducing power so that it can rapidly reduce higher concentrations of dissolved phase chlorinated solvents when injected via direct chemical reactions. Zero valent metals will continue to react with dissolved chlorinated solvents in groundwater until it is completely oxidized by chlorinated solvents, oxygen, or other oxidants that contact residual concentrations of zero valent iron. Under normal environmental conditions, zero valent metals are capable of being oxidized and reduced back and forth. The oxygen scavenger also promotes an anaerobic environment, stimulating the microorganisms.

With the addition of an electron donor source to provide hydrogen, the biodegradation process is initiated. An organic hydrogen donor such as a polylactate ester, glycerol tripolylactate, xylitol pentapolylactate, or sorbitol hexapolylactate, lactates, acetate, propionates, sugars, glucose, etc. is now injected with the intent of being cometabolized by indigenous anaerobic bacteria to produce dechlorinating conditions necessary for indigenous anaerobic bacteria to biodegrade residual concentrations of chlorinated solvents. This slow release process is controlled over time, maintaining a slow delivery of hydrogen at low concentrations which drives the anaerobic reductions. The volatile organic acid is then metabolized by indigenous bacteria to produce hydrogen, which can then be metabolized by chlorinated solvent degrading bacteria. Organic acids, hydrogen, nutrients, and bacteria then move with groundwater, enhancing the attenuation of chlorinated solvents as they move through the aquifer over a period of months.

The above-described process is preferably carried out by an apparatus such as shown in the diagram of the FIGURE. The direction of flow is indicated by arrows where appropriate. Not shown are conventional injection rods well-known in the art suitable for subsoil injections which are attached to an injection line in fluid communication with the discharge port

25. An embodiment of the inventive process begins by first filling the bioslurry tanks LT1 and LT2 and filling the feed tanks T1 and T2. A source of gas such as nitrogen or carbon dioxide is connected to inlet 21 and a water supply is connected to liquid inlet 23. Valves V7 and V8 are opened which engage an electric actuator to fill bioslurry tanks LT1 and LT2. The micro-nutrients/sodium sulfate is then manually added to the bioslurry tanks LT1 and LT2 and allowed to mix. Valves V7 and V8 are closed along with disengaging the actuator when the bioslurry tanks are filled.

Next, a pre-mixed heated lactate including vitamins B2 and B12 is manually poured into feed tank T1. Valves V5, V6, V4, and V3 are then opened. Next, pump P2 is activated and tank T2 is filled with an appropriate volume of the bioslurry. All valves are closed when finished. The tops are then secured on



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both feed tanks T1 and T2 and afterward valves V10 and V11 are opened to pressurize both feed tanks. After the injection rod has been properly placed at a selected location, the injection line is secured to discharge port 25 and valve V9 is opened.

The injection process begins when valve V1 is opened to create the injection pathways until a significant pressure drop is observed at the injection pressure vessel 31 which is filled with the source of compressed gas, preferably either nitrogen or carbon dioxide. Valve V1 is then closed and valve V3 is opened to introduce the bioslurry mixture into the subsurface pathways from feed tank T2. Valve V3 is closed when feed tank T2 is empty.

Next, pump P2 is once again activated and tank T2 is filled with more of the bioslurry. Zero valent metal is then manually added and mixed with the bioslurry in tank T2. This mixture is then injected into the subsoil from tank T2 in the same way as the previous injection of the bioslurry mixture alone.

Now valve V2 is opened to introduce the lactate mixture into the subsurface from tank T1 and is closed after the tank is empty. Valves V4, V5, and V6 are then opened to directly deliver bioslurry from tanks LT1 and LT2 into the subsurface. All valves are closed when the desired amount of bioslurry has been injected. Finally, in order to cleanse the injection line of the viscous polylactate ester or other organic hydrogen donors, more reducing agent slurry is once again injected from tank T2 having been transferred there from tanks LT1 and LT2 as previously described. With the injections complete, a post injection line purge is performed by opening valves V9 and V1 and injecting gas to clear the lines of any remaining reducing agents. With the lines cleaned, the process is complete and the next injection location is prepared.

In accordance with the invention, a test was carried out and the following results observed. A site known to be contained with chlorinated solvents was geologically mapped. After determination of the subsurface contaminate concentrations, characteristics and the direction of flow of groundwater, a series of injection points were drilled. Contaminate concentrations of cis-1,2-DCE prior to the biodegradation process ranged from 6.6 ppb to 69 ppb. The initial concentration of VC ranged from 0.97 to 2 ppb. The initial concentration of TCE ranged from 0.23 to 12.0 ppb.

After determining the levels of the contaminants, biodegradation was initiated and maintained by the addition of iron powder, lactate, reducing agents, vitamin stimulants, and delivered by compressed gases and results were observed after four months. Iron powder was chosen for two primary reactions with chlorinated solvents, the first being the anaerobic iron corrosion reaction in which water is dissociated to form hydrogen gas, and the direct absorption of a chlorinated hydrocarbon onto the surface of the iron, followed by reductive dehalogenation. Four mechanisms are at work during the reductive process. First, the zero valent metals act as a reductant by supplying electrons directly from the metal surface to an absorbed halogenated compound. Next, hydrogen gas is generated by the anaerobic corrosion of the metallic iron by water. Third, metallic iron may act as a catalyst for the reaction of hydrogen with the halogenated hydrocarbon using the hydrogen produced on the surface of the iron metal as the result of anaerobic corrosion with water. Fourth, solubilized ferrous iron can also act as a reductant, albeit at a rate at least an order of magnitude slower.

At the end of the four month process, microbial processes are strongly active as demonstrated by the disappearance of tetrachloroethane, 1,1-TCA, and dichloromethane. The alkaline conditions over the four months would suggest that the chloride production observed is primarily due to the microbial dechlorination process. The 4,600 ppb increase in chlorides observed over the period suggest significant microbial activity. There appears to be no toxicity issues in any of the

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areas on site and there has not been any microbial accumulation of intermediates of the degradation pathways. As a by-product of the program, benzene has also been addressed in those areas where it has been found in the groundwater samples.

Therefore the foregoing description of the invention demonstrates that it provides a method for accelerated dechlorination of matter contaminated with chlorinated solvents utilizing mechanisms associated with zero valent metal oxidation. It shows that with the combination of organic acids, hydrogen donors, oxygen scavengers, nutrients and zero valent metal, when added to matter contaminated with chlorinated solvents, can provide a reducing environment. Thus, the compounds disclosed have shown great utility in aiding the destruction or inactivation of chlorinated solvents. The invention also confirms that zero valent metal, when added with other compounds which provide a source of electron donors, nutrients, and reducing agents, will stimulate naturally occurring microorganisms while oxidizing dissolved phase target compounds via the surface action of the iron particles resulting in the breakdown of chlorinated solvents.

It should be understood that there may be other modifications and changes to the present invention that will be obvious to those of skill in the art from the foregoing description, however, the present invention should be limited only by the following claims and their legal equivalents.

The invention claimed is:

1. A method for accelerated anaerobic dechlorination of subsoil matter, comprising the steps of:

supplying a mixture including a zero valent metal into soil pathways to biologically react with the dissolved chlorinated solvents in the groundwater; and

supplying an organic hydrogen donor into the soil pathways to produce dechlorinating conditions such that indigenous anaerobic bacteria biodegrade residual concentrations of chlorinated solvents.

2. The method of claim 1 further including the step of supplying a reducing agent into said soil pathways to remove oxygen from groundwater and soil moisture.

3. The method of claim 1 wherein the steps of supplying said mixture and said organic hydrogen donor are carried out by placing an injection rod into the soil and then injecting them under pressure through an injection rod.

4. The method of claim 3 further including the preliminary step of injecting a gas under pressure through said injection rod and into said soil to establish preferential delivery pathways therein.

5. The method of claim 2 wherein said reducing agent is sodium sulfite.

6. The method of claim 1 wherein said organic hydrogen donor further includes vitamins B2 and B12.

7. The method of claim 1 wherein the mixture further includes nutrients.

8. The method of claim 7 wherein said nutrients are organic ammonia and ortho-phosphate.

9. The method of claim 1 wherein said organic hydrogen donor is from the group consisting of lactate, propionate, chitin, butyrate, acetate, sugars, glycerol tripolylactate, xylitol pentapolyolactate, and sorbitol hexapolyolactate.

10. The method of claim 4 wherein said gas is from the group of nitrogen and carbon dioxide.

11. The method of claim 1 wherein said mixture including a zero valent metal is a colloidal suspension in a sodium sulfite solution.

12. The method of claim 3 further including, after the step of injecting the organic hydrogen donor, an additional step of

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injecting into the soil a sodium sulfite and nutrient solution to provide for further in-situ mixing and penetration of anaerobic stimulating products.

13. The method of claim 4 further including a final step of gas injection to clear said injection rod and fluid conduit lines connected thereto.

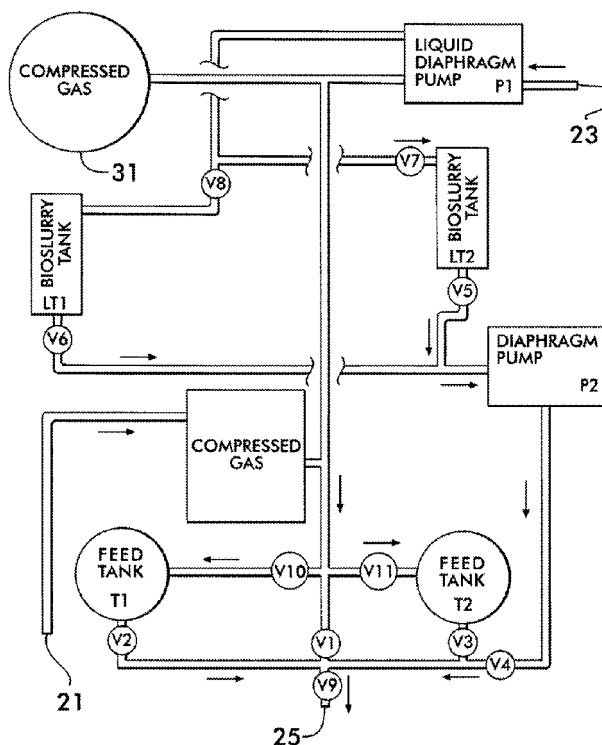
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14. The method of claim 1 wherein said metal is iron.

15. The method of claim 1 wherein said metal is in a colloidal suspension.

16. The method of claim 15 wherein the colloidal suspension includes a reducing agent.

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**EX PARTE  
REEXAMINATION CERTIFICATE**

THE PATENT IS HEREBY AMENDED AS  
INDICATED BELOW.

**Matter enclosed in heavy brackets [ ] appeared in the patent, but has been deleted and is no longer a part of the patent; matter printed in italics indicates additions made to the patent.**

ONLY THOSE PARAGRAPHS OF THE  
SPECIFICATION AFFECTED BY AMENDMENT  
ARE PRINTED HEREIN.

Column 5, line 60-column 6, line 5:

At the end of the four month process, microbial processes are strongly active as demonstrated by the disappearance of tetrachloroethane, [1,1-TCA] *1,1-DCA*, and dichloromethane. The alkaline conditions over the four months would suggest that the chloride production observed is primarily due to the microbial dechlorination process. The 4,600 ppb increase in chlorides observed over the period suggest significant microbial activity. There appears to be no toxicity issues in any of the areas on site and there has not been any microbial accumulation of intermediates of the degradation pathways. As a by-product of the program, benzene has also been addressed in those areas where it has been found in the groundwater samples.

AS A RESULT OF REEXAMINATION, IT HAS BEEN DETERMINED THAT:

Claims 1-4 are determined to be patentable as amended.

Claims 5-12, 14-16, dependent on an amended claim, are determined to be patentable.

New claims 17 and 18 are added and determined to be patentable.

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Claim 13 was not reexamined.

1. A method for accelerated anaerobic dechlorination of subsoil [matter], comprising the steps of:

supplying a mixture including a zero valent metal into [soil] permeable pathways in the subsoil that chlorinated solvents have migrated to in order to [biologically react with the] *reduce concentrations of dissolved chlorinated solvents in [the] groundwater via chemical reactions with a surface of the zero valent metal providing a hydrogen source via hydrolysis of the groundwater at the surface of the zero valent metal and evolution of hydroxides*; and

supplying an organic hydrogen donor into the [soil] permeable pathways to *provide a hydrogen source via the fermentation of the organic hydrogen donor and produce dechlorinating conditions such that indigenous anaerobic bacteria biodegrade residual concentrations of chlorinated solvents, wherein combined use of the zero valent metal and the organic hydrogen donor together in the permeable pathways accelerate dechlorination of contaminants in the subsoil and dechlorinate intermediates of the chlorinated solvents.*

2. The method of claim 1 further including the step of supplying a reducing agent into said [soil] permeable pathways to remove oxygen from groundwater and soil moisture.

3. The method of claim 1 wherein the steps of supplying said mixture and said organic hydrogen donor are carried out by placing an injection rod into the [soil] subsoil and then injecting them under pressure through [an] *the injection rod into the permeable pathways.*

4. The method of claim 3 further including the preliminary step of injecting a gas under pressure through said injection rod and into *the permeable pathways in said [soil] subsoil* to establish preferential delivery pathways [therein].

17. *The method of claim 1, wherein the intermediates include cis-1,2-DCE.*

18. *The method of claim 1, wherein the intermediates include vinyl chloride (VC).*

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